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COMPLEX DECAY OF CRYSTALLINE ORGANIC PHOSPHORS

Dr. K. Meyer and Dr. A. Maier of the Physical Institute of the University of Basel, Switzerland, have recently demonstrated that the emission of light from stilbene and anthracene phosphors is a more complex phenomenon than has been previously supposed. Their investigations have shown the presence of two new decay constants associated with the luminescence of each phosphor. The experimental procedure has been to expose the phosphor to nuclear gamma radiation and to photograph each main pulse and any associated after-pulses observed on an oscilloscope having a 10^{-8} sec. rise time. Photomultipliers used in the measurement were 19 stage tubes manufactured by Dr. N. Schaetti at the E.T.H. in Zurich (See Technical Report ONRL-13-53). These multipliers employ a focussing dynode structure and are remarkably free from after-pulses. The instantaneous output current of the photomultiplier was presented to the oscilloscope in the form of the voltage developed across a resistor having the characteristic resistance (50 ohms) of the connecting coaxial cable. Thus very narrow pulses were obtained and consequently small pulses could easily be distinguished from preceding large ones. (It was observed that most of the after-pulses were quite small corresponding to emission of a single photoelectron from the cathode of the multiplier).

The results obtained at Basel show that in addition to the presently recognized half-lives for light emission of about 0.01μ sec. (relative intensity 100 units) and about 60μ sec. (relative intensity 4.3), stilbene has two other half lives of about 0.04μ sec. and 0.83μ sec. These are each present with a relative intensity of the order of that of the 60μ sec. period. Similarly anthracene displayed two new half-lives of 0.15μ sec. (relative

intensity 3.6) and 1.31 μ sec. (relative intensity 3.2) in addition to the known half-lives of about 0.03 μ sec. (relative intensity 100) and about 30 μ sec. (relative intensity 5.6).

In contradistinction to the behavior of the crystalline organic scintillators investigated, Meyer and Maier observed that a saturated solution of terphenyl in xylene has few after-pulses. They estimated the number as eight percent of those in stilbene, and suggest that the resonance nature of the process by which the energy of excitation is communicated from the solute to the fluorescent molecules of the solvent in the liquid organic phosphors tends to promote the excitation of only a single level in the solvent molecules. Therefore the decay of the fluorescence will be more nearly a single exponential characteristic of one excited level.

It is expected that a more complete description of this work will shortly be published in *Helvetica Physica Acta* and will include a description of the experimental precautions taken to demonstrate that the photomultiplier was not responsible for a substantial number of the after-pulses observed.

AN IMPROVED GRAVIMETER

Dr. R.L.G. Gilbert (Cambridge) is building an improved gravimeter with which he plans to measure the gravitational field of the earth at depths up to 10,000 ft in the bore-hole of an oil well. The gravimeter consists of a 5 cm long beryllium-copper filament carrying an 80 gm weight at the bottom end. The filament vibrates transversely in the fundamental mode like a violin string, since the lower end is effectively held rigid by the inertia of the weight. When the gravitational field increases, the weight becomes heavier, thus increasing the tension on the filament and thereby the frequency of vibration. This idea is due to Bertrand (*Comptes Rendus*, 207, 356), and has been described in an earlier version by Gilbert (*Proc. Phys. Soc.* B62, 605 (1949)). It has the important advantage over spring gravimeters that the frequency is nearly independent of the mechanical properties of the supporting strip, and accordingly it displays a much higher stability.

The filament vibrates at about 1000 cycles per second and is driven at constant amplitude by an oscillator, the frequency of which is derived from the vibration itself.

An important improvement has been made in the latest model by partially supporting the weight with a hinge at one side. The point of attachment of the filament lies below the center of gravity of the weight and closer to the hinge. When the temperature increases, increasing the length of the filament, the tension is thereby increased because of the increased torque offered by the weight. The change in length and the change in tension have an opposite influence on the frequency and accordingly the temperature coefficient is much reduced.

The frequency of oscillation of the filament is compared with a standard frequency stepped down from a quartz crystal oscillator. The beating between the two frequencies is used to drive an electric clock and the rate of this clock is then a measure of the change in the gravitational field. Since the clock will run either way, its average rate gives the desired indication even if there are severe fluctuations, for instance those due to vibration of the supports.

Dr. Gilbert estimates that the new bore-hole instrument will give a precision of ± 0.3 milligals and may be within ± 0.1 . The former is the equivalent of the gravitational change in going down 10 ft in rock. The first tests of the new instrument are to be held this summer. Further information can be obtained from Technical Report ONRL-69-53, available from the Technical Information Section, Code 740, Office of Naval Research, Washington 25, D.c.

LOW NOISE AMPLIFIER

Mr. P. J. Baxandall of the Telecommunications Research Establishment, Great Malvern, Worcestershire, has built an amplifier whose noise is the equivalent of the Johnson noise from a 2 ohm resistor at a temperature of 20°K. The instrument was designed for use in electrical measurements encountered in cryogenic experiments, for instance, with low temperature bolometers. The band pass of the instrument extends from 100 to 4,000 cycles.

The distinctive novelty in the amplifier is the use of a preliminary transformer within the cryostat at low temperature. This is a specially wound transformer with an input impedance of about 0.5 ohms and an output of 300 ohms. The core is of mumetal whose effective permeability at 20°K is about one-third of its room temperature value. A second transformer is used at room

temperature in the amplifier operating from 300 ohms up to 1 megohm. This second transformer was specially wound to achieve a low series resistance with a high eddy-current shunt resistance. The eddy-current shunt resistance is about 40 megohms when referred to the secondary of the high impedance transformer, and this resistance is the principal source of noise.

The first tube is a Mullard ME 1400, sometimes called "the poor man's electrometer tube". It is operated under electrometer conditions with a grid current of less than 10^{-11} amperes.

THE INFRARED ABSORPTION SPECTRUM OF THE OXONIUM ION

Dr. N. Sheppard and Mr. D. Bethel (Cambridge) have recently succeeded in observing the infrared absorption spectrum of the oxonium ion CH_3^+ . Two absorption bands were clearly located at 1134cm^{-1} and 1670cm^{-1} respectively, while a very broad, unresolved band extends from 2600 to 3300cm^{-1} . These frequencies are consistent with the pyramidal model for this ion and exclude a planar one. The oxonium ion is isoelectronic with the neutral NH_3 molecule and the corresponding normal modes of vibration agree closely in these two molecules.

The spectra were observed on a capillary layer of an equimolar mixture of nitric acid and water, between flat silver chloride plates at low temperatures. The observations show that previous attempts to observe the spectrum of the oxonium ion failed primarily because, due to the very strong absorption, extremely thin layers have to be used. Preliminary results on an equimolar mixture of perchloric acid and water confirm the above results.

These observations are thus in excellent agreement with the conclusions of Richards and Smith based on the nuclear magnetic resonance spectra of a number of inorganic hydrates (Trans. Far. Soc. 48, 307 (1952)).

THE INFRARED ABSORPTION SPECTRUM OF CARBON DIOXIDE AT HIGH PRESSURES

The infrared absorption spectrum of carbon dioxide was studied at pressures up to 85 atmospheres by Prof. J.A.A. Ketelaar (Dept. of Phys. Chem., Amsterdam), in collaboration with the high pressure laboratory of

Professor A. Michels. A Perkin-Elmer instrument was used to obtain the spectrum of carbon dioxide contained in a high pressure steel chamber with rock salt windows. Several normally forbidden transitions were found to occur when the pressure of the gas inside the cell was approximately 20 atmospheres or greater and some of these are listed below. Their existence is due to the increased probability of collisions between molecules at these high pressures, resulting in perturbation of the symmetrical linear structure of the molecule. In agreement with this explanation the normally forbidden lines are also found in mixtures of carbon dioxide and inert gases, such as argon, at high pressures.

The newly observed, pressure-induced infrared absorption bands include the symmetrical stretching frequency at 1340cm^{-1} , and bands at 2663cm^{-1} , 2840cm^{-1} , 3016cm^{-1} and 1680cm^{-1} . These last two can be interpreted as the combination and difference bands of the normally infrared active bands at 667 and 2349cm^{-1} .

The normal transitions found in the infrared are directly proportional to the pressure but these forbidden transitions have been found to be proportional to the square of the pressure. This makes it easy to identify each type of transition. It is also found that with increasing temperature the intensity of these new lines decreases, instead of increasing as one would expect from the greater translational energy of the molecules. This effect cannot be explained at present.

INORGANIC COMPOUNDS CONTAINING THE NO_2^+ ION

Several compounds which are of interest as nitrating agents have been studied by Prof. C.H. MacGillavry and co-workers (University of Amsterdam). The most recent of these are the $\text{N}_2\text{O}_5 \cdot 3\text{SO}_3$ molecule and the $\text{HNO}_3 \cdot 3\text{SO}_3$ molecule. These have been studied by the usual single-crystal X-ray techniques, and it has been shown that the first of these compounds consists of ions of NO_2^+ and $\text{S}_3\text{O}_{10}^{2-}$. The unit cell is monoclinic. The $\text{HNO}_3 \cdot 3\text{SO}_3$ molecule has been shown to consist of NO_2^+ and $\text{HS}_3\text{O}_{10}^-$ ions and to have a triclinic unit cell. The most interesting thing about these structures is that they all seem to contain the NO_2^+ ion, which has been suggested as the active agent in nitrating reactions by several investigators, notably by Prof. C.K. Ingold (London). The complete details of these structure

determinations will be published in Acta Crystallographica in the near future.

SYMPOSIUM ON ELECTROLYTES IN ORGANIC SOLVENTS

A one-day symposium on "Solutions of Electrolytes in Organic Solvents" was held at Buckland House (Buckland, near Harwell) on Wednesday, 15 April, under the auspices of the Atomic Energy Research Establishment. This meeting was organized by Dr. E. Glueckauf and Dr. N. N. Greenwood (AERE). Some of the results of the symposium are presented in the following paragraphs. A more complete account of the discussion is given in Technical Report ONRL-63-53, available from the Technical Publications Office, Office of Naval Research, Code 740, Washington 25, D.C.

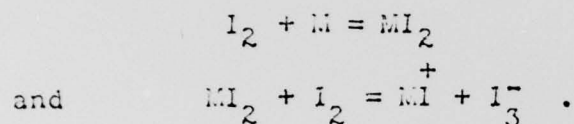
Extraction of Metal Nitrates into Phosphate Esters

T. V. Healy and G. M. Waind (AERE) discussed their work on the extraction of cobalt and sodium nitrates from aqueous solutions by tri-n-butyl phosphate (TBP), and their study of the partition of uranyl nitrate between water and the solvents TBP, di-n-butylphenyl phosphate (DBPP) diphenyl-n-butyl phosphate (DPBP) and tri-phenyl phosphate (TPP).

The organic phase was treated as an ideal solution up to concentrations of about 0.1 molal, and the thermodynamic equilibrium constants and free energy changes of transfer of uranyl nitrate from TBP to the other solvents were calculated. TBP was found to be the best solvent for all of the salts studied; considerations of the electron donor ability of the respective organic solvents indicate that this result should be expected. The deviations from ideal behavior above concentrations of 0.1 molal were used to obtain an approximate solvation number for the complexes between uranyl nitrate and the organic solvents (e.g. $n = 2$ for the complex $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$). Values of n calculated from the activities in concentrated solutions varied from $n = 2.0$ for TBP to $n = 3.2$ for DPBP. Treatment of the diluent partition data below 0.1 molal nitrate in the organic phase, in conjunction with the solvent activities, gave solvation numbers which were in fair agreement with the approximate values obtained at higher concentrations in the pure solvents.

Iodine Solutions

The complexes formed in iodine solutions were the subject of several studies and provided some interesting new results. Of most interest was Greenwood's work which developed a complete correlation between the color, electrical conductivity, and reactivity of the solutions. For instance, no violet solution of iodine (designated type A) conducts electricity, whereas all brown solutions (designated type B) conduct ionically as a result of the dissociation



In these latter solutions the iodine cation is stabilized by the solvents due to the electron donor-acceptor mechanism, which is consistent with the older solvation theory. The following observations were given by Greenwood to develop further this correlation using iodine as an example, but experiments show that bromine and the two interhalogens, iodine monochloride and iodine monobromide, behave analogously.

(a) Addition of a type B solvent to a violet, non-conducting solution progressively shifts the wavelength of maximum absorption; the solution gradually turns brown, with a simultaneous onset of conductivity which increases with continued addition of the ionizing solvent.

(b) The electrical conductivity of a brown solution decreases with rise in temperature, the color of the solution simultaneously changing from brown towards violet. On lowering the temperature, the conductivity increases again and the solution regains its brown color.

(c) In solvents which are able to stabilize the ionic form of the solute but have an insufficiently high dielectric constant to effect ionic dissociation, there is a considerable increase in the apparent dipole moment of iodine, and solutions are intermediate in color between violet and brown (Fairbrother).

(d) Ionic reactions typical of either the iodine cation or the polyhalide anion occur rapidly in brown solutions but not in violet solutions.

It was concluded that the halogens and interhalogens are only non-electrolytes in solvents of type A.

ELECTRICAL RESISTIVITY DUE TO VACANCIES IN COPPER

An informal conference on Lattice Defects and the Electrical Resistivity of Metals held at Birmingham University on 24-25 April included a number of important papers on both experimental and theoretical work. A review of the proceedings is given in Technical Report ONRL-56-53 available from the Technical Publications Office, Code 740, Office of Naval Research, Washington 25, D.C. In the following, one of the contributions is summarized.

Mr. P. Jongenburger (Philips, Eindhoven) has calculated the electrical resistance due to vacancies in monovalent metals by the method first used by Mott to calculate the resistance due to substitutional impurities in copper (Proc. Camb. Phil. Soc. 32, 281 (1936)). This method has recently been improved by Friedel (see ONRL-50-53). The three principal assumptions entering the calculation are (1) the valence electrons in copper are essentially free, (2) the scattering function, V , is a function of r only, where r is the distance from the center of the vacancy, (3) there is no interaction between lattice vibrations and terms due to the vacancy, i.e., Matthiessen's rule is applicable.

First a scattering potential, $V(r)$ is chosen; then the asymptotic phases, α_l , of the radial wave functions are computed. The scattering cross section of the vacancy is calculated from the asymptotic phases. The potential, $V(r)$, is a self-consistent solution if the α_l derived from it satisfy

$$-1 = n = \frac{2}{\pi} \sum_l (2l + 1) \alpha_l(k_F), \quad (1)$$

the last equality having been proved by Friedel. Here k_F is the momentum corresponding to the Fermi energy, and n is the amount of charge displaced from the vicinity of the vacancy. Equation (1) states that one unit of charge is displaced from the conduction band in the vicinity of the vacancy.

The scattering potential which was chosen to represent the vacancy is the negative Hartree field for Cu, which was fitted by the analytic form

$$V(r) = 27r^{-1} e^{-2.5r} \text{ atomic units.} \quad (2)$$

The value for n came out equal to -0.95, so that the

potential is not quite self consistent; the electrical resistivity of vacancies, calculated from (2), is $\rho = 1.25\mu\Omega/\text{atom per cent vacancies}$. A second scattering potential, namely a rectangular one, was also used; the results are summarized below:

$V(r)$	n	ρ
negative Hartree	-0.95	$1.25\mu\Omega/\text{atom per cent vacancies}$
rectangular	-1.00	1.35

Thus it appears that no further refinement is necessary and $\rho = 1.3\mu\Omega/\text{atom per cent vacancies}$ in Cu.

For both Au and Ag the resistivity computes to be $\rho = 1.5\mu\Omega/\text{atom per cent vacancies}$. These results, compared with experimental data for the effects of elements in alloys, show that vacancies in these monovalent metals act very much like substitutional Ni in Cu, and Pt in Au: not at all, however, like Zn in Cu, and Hg in Au.

A DUAL CAPACITY MAGNETIC DRUM

At the Telecommunications Research Establishment in Great Malvern, England, a group under the direction of Dr. A. M. Uttley has developed a high speed electronic computer, parallel in operation, having a high speed cathode ray tube store with a capacity of 512 words of twenty-four digits, and an auxiliary magnetic drum store which can operate in either one of two modes. In the first mode the drum has a capacity of around 50,000 digits and in the second mode a capacity of over a million and a half digits.

This novel feature of dual capacity is accomplished by having the twenty-four recording and reading heads mounted on a bridge which can be held either fixed in position or allowed to oscillate as the drum rotates. In the first mode, that is, where the bridge is held fixed, each track has a capacity of 2,048 digits making a total capacity of 49,152 digits. In the second mode, the bridge is allowed to oscillate so that each track has a length of thirty-two turns; thus the capacity of each track is 65,536 digits giving the drum, for all twenty-four tracks, a total storage capacity of 1,572,864 digits. The mean access time for the first mode is 20 milliseconds and for the second mode is 1.25 seconds. There is no mutual interference between the tracks of the two modes.

The drum is four inches in diameter and coated with iron oxide.

The above development was reported at the Symposium on Automatic Digital Computation held at the National Physical Laboratory, Teddington, on 25-28 March 1953. Technical Report ONRL-64-53, a report discussing some of the topics presented at this Symposium, is available from the Technical Publications Office, Code 740, Office of Naval Research, Washington 25, D.C.

THE DEKATRON TUBE AS A COMPUTING ELEMENT

At the Royal Aircraft Establishment, Farnborough, England, a group has developed a computing machine, primarily for the purpose of data reduction, which uses as its main computing element a dekatron tube. This is a gas-filled cold-cathode tube in which the discharge is arranged between a central anode and one of ten surrounding cathodes. In order to apply the tube to computing work, nine of the cathodes are connected internally and the tenth cathode left separate in order that it can provide a carry pulse. The principal of operation of the dekatron tube has been described in ESN 5, 272 (1951); a more detailed presentation has been given by J. R. Acton, "The Single-Pulse Dekatron", Electronic Engineering XXIV-288, 48 (1952).

The particular tube used in this computer has a stepping frequency of 20,000 steps per second. This resolving time of fifty microseconds required to step the discharge from one cathode to another must be broken up into pulses of twenty-five microseconds duration spaced a minimum of twenty-five microseconds apart. The dekatron tube is so constructed that the position of the discharge can be viewed from the end of the tube; this has the advantage that if the machine has met a fault, the contents of the various registers can be read immediately without additional test equipment.

Employing these tubes in arithmetic units of parallel circuitry, as has been done in the case of this machine, does not necessarily bring about a low speed machine. In fact with the 20,000 cycle repetition rate and using short-cut methods an 8 x 8 decimal multiplication could be performed in 5.8 milliseconds. In actual fact multiplication will take 18 milliseconds, and addition 9 milliseconds owing to the fact the period of rotation of the magnetic drum store employed in this machine is 9 milliseconds.

THE EFFECTS OF TONICITY ON THE RATE OF SODIUM EXCRETION FROM HUMAN ERYTHROCYTES

E. J. Harris and T.A.J. Pranker of University College and University College Hospital, London, observed the loss of isotope from human erythrocytes which had been previously treated with a solution containing a proportion of Na^{24} and then placed in a saline bath at 30°C . The cells were centrifuged at 3000 g under standard conditions so that any Na^{24} loss from the cells would be a constant fraction of the whole. The transfer of Na^{24} out of the cells to a solution practically free from Na^{24} follows, as a rule, simple first-order kinetics. The rate constant, which is found from the slope of a plot of $\log (\text{Na}^{24} \text{ content})$ against time, applies to unit volume of cell fluid. To obtain the permeability constant, which refers to unit area, it is necessary to multiply by the ratio of volume of internal fluid to surface area. Measurements have been made of the rate constant in iso- and hypotonic media (0.9 - 0.6% NaCl); in the latter it is reduced nearly in the proportion by which the fluid volume becomes increased due to swelling. As the surface area remains nearly constant this result means that the permeability constant is not changed by the swelling consequent upon use of a hypotonic solution. Restoration of isotonicity, which leads to reversion to the original volume, also brings about a return to the original rate constant. If the experiments are so conducted that observations of Na^{24} content are made for some time before addition of the water (which causes hypotonicity) and the observations are continued until after the restoration of isotonicity (by addition of NaCl), it is found that the entry of water at the time of swelling, and its exit at the time the cell shrinks, does not induce a sudden change of the Na^{24} content. Thus the cells can gain, and later lose, water equal in these experiments to a maximum of 40% of their ordinary water content without bringing about any abnormal sodium transfer.

EFFECT OF MAGNESIUM IONS ON THE RELEASE OF ACETYLCHOLINE

O. F. Hutter and Krista Kostial of University College, London, in order to test the effects of magnesium ions on the output of acetylcholine from the cholinergic nerve endings, used perfused preparations of the cat's superior cervical ganglion. The preganglionic nerve was stimulated with supramaximal shocks at a frequency of 2 per sec for 5 out of every 10 min. In this way a series of samples containing approximately equal amounts of

acetylcholine could be obtained. Addition of magnesium chloride (15 mM) to the perfusion fluid (Ringer-Locke's solution containing 1:100,000 eserine sulfate) reduced the amount of acetylcholine in the perfusate to about 50% its original value. With higher concentration of magnesium chloride (25 mM) no acetylcholine could be detected on preganglionic stimulation. The effects were reversible.

ION EXCHANGES IN SYMPATHETIC GANGLIA

H. McLellan of University College, London, has determined the sodium and potassium contents of freshly excised sympathetic ganglia of rats and rabbits. The values average 81 ± 14 μ equiv/g for sodium (S.E. 5 analyses) and 89 ± 23 μ equiv/g for potassium (S.E. 16 analyses). The high value for sodium has been checked by determination of the total chloride, which gives an average value of 92 ± 29 μ equiv/g (S.E. 6 analyses). If both sodium and chloride ions are assumed to be extracellular, then the extracellular space in these ganglia may comprise some 60% of the tissue weight. If this is so, then the potassium concentration within the cells could be of the order of 200-250 μ equiv/g.

The exchangeability of the ganglionic potassium has been followed with radioactive K^{42} as a tracer. The extent to which the analytically determined tissue K^+ exchanges with the K^{42} of Locke's solution in which the ganglion is incubated never exceeds 50%, and is usually of the order of 35%. It would seem, therefore, that at least one half of the tissue K either exchanges very slowly, being perhaps bound in some way to the tissue proteins, or is relatively inaccessible to the K^{42} of the bathing solution. Brief soaking in isotonic potassium phosphate solution results, however, in a complete replacement of the tissue K by the K^{42} of the medium.

Identical results have been obtained with ganglia in which the pre- or post-ganglionic fibers were cut and allowed to degenerate for three weeks.

PERSONAL NEWS ITEM

Dr. Geoffrey Gee, F.R.S., has been appointed Professor of Physical Chemistry at the University of Manchester in succession to the late Professor M.G. Evans, and will take up his duties early in the autumn. Dr. Gee has been Director of Research at the British Rubber Producers' Research Association.

TECHNICAL REPORTS OF ONRL

The following reports have been forwarded to ONR, Washington, since the last issue of ESN. Copies may be obtained from the Technical Publications Office, Code 740, Office of Naval Research, Washington 25, D.C.

ONRL-65-53 "Some Historical Notes on Experimental Psychology at Cambridge" by C. H. Graham

ONRL-66-53 "The Belgian Computer" by R. R. Weber

On 30 June 1953, Captain P. D. Lohmann, USN, who has been the Assistant Naval Attache for Research and Officer-in-Charge, Office of Naval Research, London Branch Office, London, England, for the last three years, will retire from active service in the Navy, with the rank of Rear Admiral (Ret.). Captain Lohmann will be relieved by Captain P. S. Creasor, USN.

Prepared by the Scientific Staff
Submitted by Dr. S. R. Aspinall
Deputy Scientific Director

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